

# Catalytic wet air oxidation of phenol with pelletized ruthenium catalysts

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## Abstract

The pelletized ruthenium catalysts were prepared by impregnation of different pelletized supports: CeO<sub>2</sub> and ZrO<sub>2</sub>-CeO<sub>2</sub>. Their mechanical strength, specific surface area, pore size distribution and adsorption capacity for phenol were studied. Catalytic wet air oxidation of phenol with pelletized catalyst of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> was performed in a continuous packed-bubble column reactor. The fresh and used Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts were compared. It shows that introduction of ZrO<sub>2</sub> into Ru/CeO<sub>2</sub> increased the mechanical strength, specific surface area and adsorption capacity of pelletized catalyst. In the experiment of wet air oxidation of phenol with Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> for 100 h, phenol and TOC removal stabilized around 100 and 96%, respectively. The concentrations of intermediates were low. The leaching concentrations of active species during the reaction were also low. After reaction, the textures, morphologies, microcosmic crystal pattern of catalyst and oxidation state of catalytic active phase of zirconium, cerium, ruthenium and oxygen did not change much, but the carbonaceous deposits on the surface of used catalyst were observed, and they would be fully oxidized at about 300 °C. The pelletized catalyst of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> possesses the possibility of practical use.

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**Keywords:** Catalytic wet air oxidation; Pelletized ruthenium catalyst; Ru/ZrO<sub>2</sub>-CeO<sub>2</sub>

## 1. Introduction

Catalytic wet air oxidation (CWAO) is an effective process to treat high concentrated organic wastewater, which is too concentrated for practical biological remediation and too dilute for economical incineration and recovery [1].

However, the lack of active and durable catalyst under severe reaction conditions has prevented CWAO from being implemented for environmental remediation [2].

In recent years many heterogeneous catalysts such as Ru/ZrO<sub>2</sub>, Ru/TiO<sub>2</sub>, Ru/CeO<sub>2</sub>, Mn/Ce, Pt/C and Ru/C have been studied [3–11]. Ruthenium loaded on high surface support of TiO<sub>2</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub> has been proved to be an active and stable catalyst in catalytic wet air oxidation [3–5]. It was shown that ruthenium loaded on high specific surface area ceria was one of the most active catalysts in CWAO [6,7]. However, these promising results were obtained in a batch reactor using the finely powdered ceria with a diameter of about 4 μm. As CeO<sub>2</sub>

cannot be easily pelletized, continuous processes with Ru/CeO<sub>2</sub> have not yet been taken into consideration [12]. Generally, a continuous process with pelletized catalysts is used in practical wastewater treatment plants, so it is very important to develop pelletized Ru/CeO<sub>2</sub> catalysts.

The dynamic reaction condition of catalytic wet air oxidation requires that the pelletized catalysts should possess strong mechanical strength to keep its activity in reactor, which is determined by that of supports [13]. Apparently, there are a variety of methods to determine mechanical strength of pelletized catalysts. Ismagilov et al. concluded that the stronger the pellets were, the better they resisted attrition and impact. The crushing strength and static method were recommended to evaluate the mechanical strength of pelletized catalysts by Ismagilov et al. [13].

In a dynamic reactor, the loss in catalytic activity can be attributed to the leaching of active species in the acidic reaction medium and the formation of carbonaceous deposits on the surface of catalyst during the reaction. Catalytic activity loss caused by these two factors will be noticeable only after long-time reaction. Generally, it is not easy to accurately assess the stability of catalyst through the continuous experiment in

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laboratory as the time of the experiment in laboratory is not long enough to observe obvious decrease of catalytic activity. In this case, comparison study of fresh and used catalyst will give useful information to evaluate the stability of catalyst in practical process. However, this study was rarely done for ruthenium catalysts in the continuous process. As there are also no reports about practical catalytic wet air oxidation process using the pelletized Ru/CeO<sub>2</sub>, it is also meaningful to compare the used catalyst with fresh catalyst and bring information to investigate the possibility of practical use of the pelletized Ru/CeO<sub>2</sub> catalyst.

In our research, pelletized Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts were prepared and used to oxidize phenol in a continuous packed-bubble column reactor. Comparison of fresh and used catalyst was carried out to investigate the stability of catalyst.

## 2. Experimental

### 2.1. Preparation of supports and catalysts

Fifty milliliters aqueous solution containing 0.9 mol/L Ce(NO<sub>3</sub>)<sub>3</sub> and 0.1 mol/L ZrOCl<sub>2</sub> were added dropwise into 1000 mL of 0.5 mol/L ammonia aqueous solution under vigorous stirring. After precipitation, the mixtures were filtered. The remaining precipitate was dispersed into 400 mL deionized water and a brownish slurry was obtained. The pH of the slurry was adjusted to 10 with aqueous ammonia solution (28%) and 0.6 g polyvinyl alcohol was added into the slurry. The slurry was then heated in an airproofed flask with back flow for 24 h. When the slurry was cool, it was filtered. The precipitate was developed into about 2 mm pellets using a special rubber mold, which was specifically described in our previous work [14]. The pellets were then desiccated at 100 °C for 24 h and calcined at 600 °C for 5 h. The pellet so-prepared was denoted as ZrO<sub>2</sub>-CeO<sub>2</sub>. If the aqueous solution contained only Ce(NO<sub>3</sub>)<sub>3</sub>, the pellet prepared was expressed as CeO<sub>2</sub>. Both the pellets were immersed in 6 mL RuCl<sub>3</sub> solution for 36 h at room temperature, and then dried at 100 °C for 12 h and finally calcined at 350 °C for 4 h. The different molar concentrations of RuCl<sub>3</sub> solution were used to obtain a theoretical 2 wt.% ruthenium loading for both impregnated ruthenium catalysts. The catalyst prepared was denoted as Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> and Ru/CeO<sub>2</sub>, respectively.

### 2.2. Wet air oxidation

Catalytic wet air oxidation of phenol (2100 mg/L) with Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> was performed using a continuous packed-bubble column reactor schematically described in Fig. 1. Air from a gas cylinder was pressurized to 4 MPa and its flow rate was adjusted with a mass flow controller to be 80 mL/min. Phenol solution was fed by a high-pressure pump with the flow rate of 0.5 mL/min. Air and liquid were mixed at the inlet of the reactor which was equipped with an axially located thermocouple and heated with an electrical furnace. The reactor was packed with the catalysts placed between two layers of supporting material. The internal diameter of the reactor was

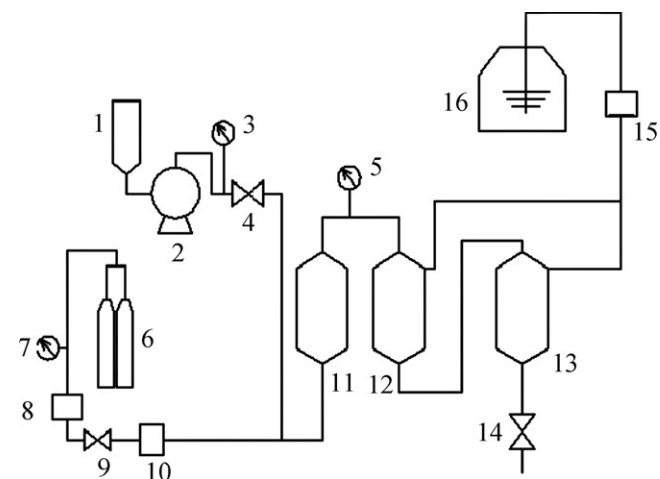


Fig. 1. The schematic diagram of dynamic experiment of wet air oxidation. (1, 13) Reservoir; (2) metering pump; (3, 5, 7) pressure indicator; (4, 9) valve; (6) gas cylinder; (8) pressure regulator; (10) mass flow meter; (11) reactor; (12) separator; (14) sampling valve; (15) back-pressure regulator; (16) absorbing device.

about 16 mm and the layer of catalyst was about 75 mm. Gas and liquid flow in co-current upflow mode through the reactor. At the reactor outlet, the liquid and gas flows were cooled and recovered in the gas-liquid separator. The gas flow was depressurized to atmosphere pressure by a back-pressure regulator. The reactor loaded with 28 g catalyst if necessary was operated at the temperature of 140 °C. Liquid samples were taken from reactor through a sampling valve. The analysis of total organic carbon (TOC), phenol, intermediates produced were carried out. The leaching concentrations of ruthenium, zirconium and cerium during the reaction were also measured through analyzing the dissolved concentration of ruthenium, zirconium and cerium in all samples.

### 2.3. Adsorption experiments

Adsorption experiments were carried out to determine the adsorption capacity of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> and Ru/CeO<sub>2</sub> for phenol at the temperature of 25 °C and atmosphere pressure in an airproofed bottle with an agitator. In the simultaneous adsorption experiments, 300 mL of 2100 mg/L phenol solution and 28 g catalysts were loaded in the bottle. At the predetermined time intervals, samples were taken and the phenol concentrations in solution were analyzed.

### 2.4. Analytical methods

The Brunauer, Emmett and Teller (BET) specific surface area was determined using a Micromeritics ASAP 2010 instrument. The mechanical strength of pelletized catalysts was measured according to National Standard of the People's Republic of China (GB3635-83) [15]. TOC was determined by Shimadzu 5000 TOC analyzer. Analysis of phenol and intermediates during the reaction was performed by high-pressure liquid chromatogram (HPLC) with a UV detector using an Inertsil ODS-3 column. The mobile phase was a

Table 1  
The characterization of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> and Ru/CeO<sub>2</sub>

Catalyst samples	BET surface area (m <sup>2</sup> /g)	Mechanical strength (MPa)	Average pore size (nm)	Pore volume (cm <sup>3</sup> /g)	pH <sub>pzc</sub>	COD removal in acetic acid oxidation after 120 min (%)
Ru/ZrO <sub>2</sub> -CeO <sub>2</sub>	103	17	3.7	0.04730	5.2	98%
Ru/CeO <sub>2</sub>	74	15	4.4	0.02496	5.4	93%

mixture of 89.91% water, 0.09% phosphoric acid and 10% methane with a flow rate of 1 mL/min. X-ray powder diffractometer (XRD) analysis was carried out in a D/max-III A powder diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the scanning range of 10–75° with a speed of 6°/min. Ru, Zr and Ce content in the catalyst was determined by sequential X-ray fluorescence spectrometer (Shimadzu, XRF-1700, Japan). The amount of zirconium, cerium and ruthenium dissolved in the sample was determined by inductively coupled plasma emission spectrometer (ICP) (Thermo Electron, IRIS Intrepid, USA). The surface morphology of catalyst was analyzed using a scanning electron microscope (SEM) of JEOL JSM-6301F equipped with energy-dispersion microanalysis system. Transmission electron microscope (TEM) studies were performed using a JEM 2010 microscope with a resolution of 0.25 nm. The presence of Ru was controlled by EDX carried out in the STEM mode. Before the analysis of XRD, TEM and Ru, Zr and Ce content of catalyst, the pelletized catalyst was grinded into powder. X-ray photoelectron spectroscopy (XPS) analysis was carried out to measure the chemical valence of the elements on the surface of the catalyst. PHI ESCA 5700 instrument, with a Al K $\alpha$  X-ray source (1486.6 eV) and pass energy of 29.5 eV operated at a pressure of  $7 \times 10^{-10}$  Torr, was used. The binding energies were calibrated with respect to the signal of contamination carbon (binding energy = 284.82 eV). The organic species on the surface of used catalyst were characterized by temperature-programmed oxidation (TPO) with the apparatus set up by ourselves using Micromeritics instruments. The catalyst was firstly purged with helium flow (30 mL/min) at 50 °C for 30 min, and then heated under a flowing gas mixture of 5% oxygen in helium (10 mL/min). Temperature was raised at a rate of 10 °C/min. Analysis of the gaseous burn-off products was performed by thermal conductivity (TCD) and by quadrupole mass spectrograph (MSC 200).

### 3. Results and discussion

#### 3.1. Effect of incorporation of ZrO<sub>2</sub> into CeO<sub>2</sub> on the catalyst performance

One of the most widely used methods to increase the mechanical strength of supports and catalysts is chemical modification with various compounds [16]. The modifier must be stable in the acidic reaction medium of wet air oxidation. However, many compounds were reported to be unstable at acidic reaction media in wet air oxidation [3]. According to the above description, only TiO<sub>2</sub> and ZrO<sub>2</sub> are stable and readily

available supporting materials. It was reported that the redox behaviour of cerium oxide can be severely modified by incorporation of zirconium into CeO<sub>2</sub> lattice [17]. ZrO<sub>2</sub> was selected as the modifier.

The crushing strength of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> and Ru/CeO<sub>2</sub> is listed in Table 1. Ismagilov et al. reported that the mechanical strength of pellets should exceed 10 MPa to avoid crushing under dynamic conditions [13]. The mechanical strength of both pellets was more than 10 MPa.

There are many molding methods to prepare Al<sub>2</sub>O<sub>3</sub> pellet, which is helpful for developing CeO<sub>2</sub> or CeO<sub>2</sub>-based pellets [18]. In most methods pellets were prepared from powder. In

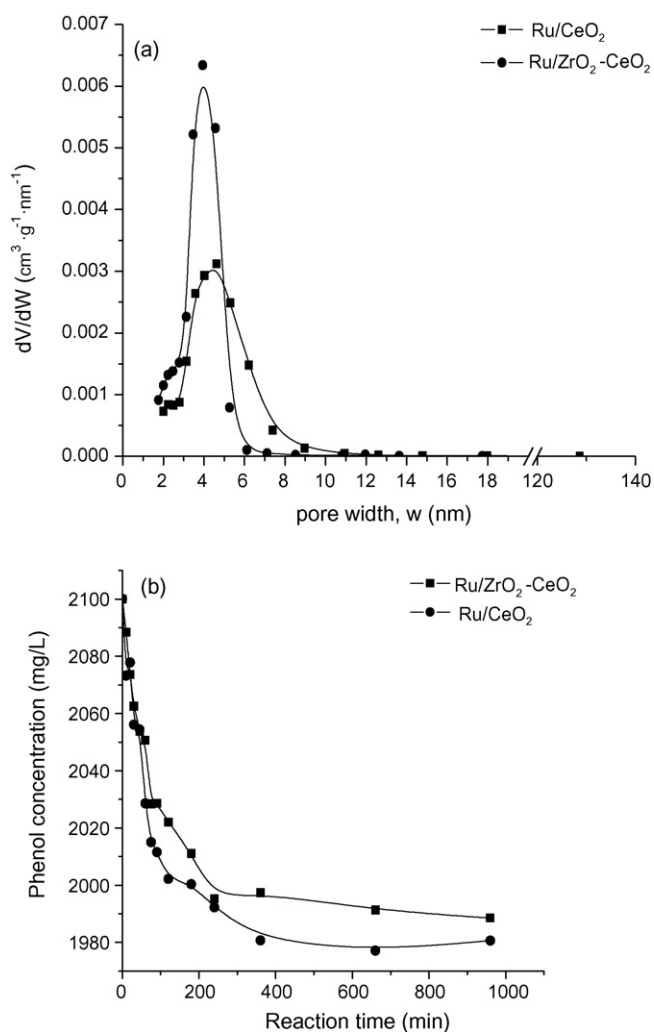


Fig. 2. Pore size distribution and adsorption process of Ru/CeO<sub>2</sub> and Ru/ZrO<sub>2</sub>-CeO<sub>2</sub>. (a) Pore size distribution; (b) adsorption process.

our experiment, pellets were prepared from precipitate, which was actually gel. During the desiccation, surface tension and capillary force come into being as the evaporation of the solvent in micropore of the gel, which can cause the contraction of pellet. The contracted pellet possesses strong mechanical strength. When the contracted pellet was calcined at 600 °C, the small precursor particles, which are not well defined, will crystallize. Some unstable crystals will re-crystallize. All of these will increase the mechanical strength of pellet. The process of back flow and polyvinyl alcohol added can enhance the stability of the gel. During calcination, the volatilization of gas caused by the decomposition of polyvinyl alcohol can increase the number of micropores and specific surface area of the pellet. In the case of preparation of pellet from powder, the crystallites are already formed and the calcination temperature should be higher to produce the equal mechanical strength. It is well known that if the calcination temperature is too high, the specific surface area will decrease because of sintering. Pellets in our experiment were prepared from gel but not from powder.

From Table 1 it is seen that introduction of ZrO<sub>2</sub> into CeO<sub>2</sub> can increase the mechanical strength of catalyst. This increase is due to the interaction between cerium compounds and modifying additive of zirconium. The BET specific surface area of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> is larger than that of Ru/CeO<sub>2</sub> (Table 1). Thus, doping ZrO<sub>2</sub> into CeO<sub>2</sub> can increase not only mechanical strength but also specific surface area of the pelletized catalyst. In the field of three-way catalyst, there was an established fact that introduction of ZrO<sub>2</sub> into CeO<sub>2</sub> can enhance the specific surface area of oxide powder after calcination at high temperature [17].

One of the important steps in catalytic reaction is adsorption and the two most important adsorbent properties are surface chemistry and pore size distribution [19]. The difference of the iso-electric point between both catalysts is not obvious (Table 1). Fig. 2a illustrates the pore size distribution of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> and Ru/CeO<sub>2</sub> and Table 1 summarizes average pore size and pore volume of them. Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> has significant

volume of pores in the 2–7 nm range. Ru/CeO<sub>2</sub> has significant volume of pores in the 2–9 nm range. The pore volume of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> was larger than that of Ru/CeO<sub>2</sub>. Fig. 2b demonstrated the adsorption processes in phenol solution with

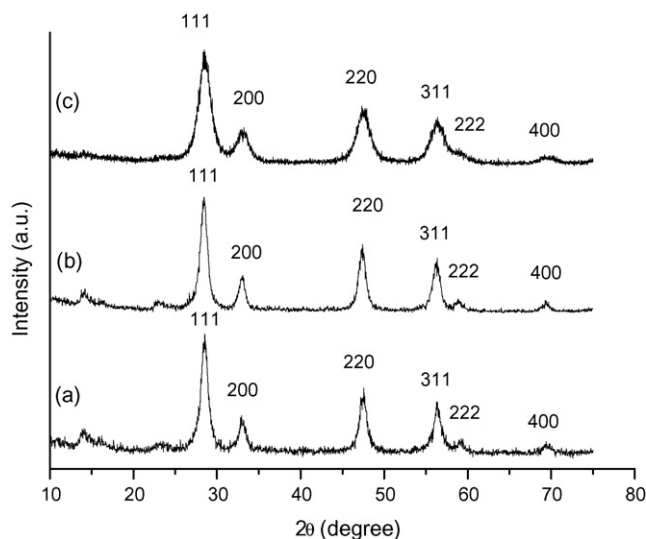


Fig. 3. XRD pattern of different catalysts. (a) Fresh Ru/ZrO<sub>2</sub>-CeO<sub>2</sub>; (b) fresh Ru/CeO<sub>2</sub>; (c) used Ru/ZrO<sub>2</sub>-CeO<sub>2</sub>.

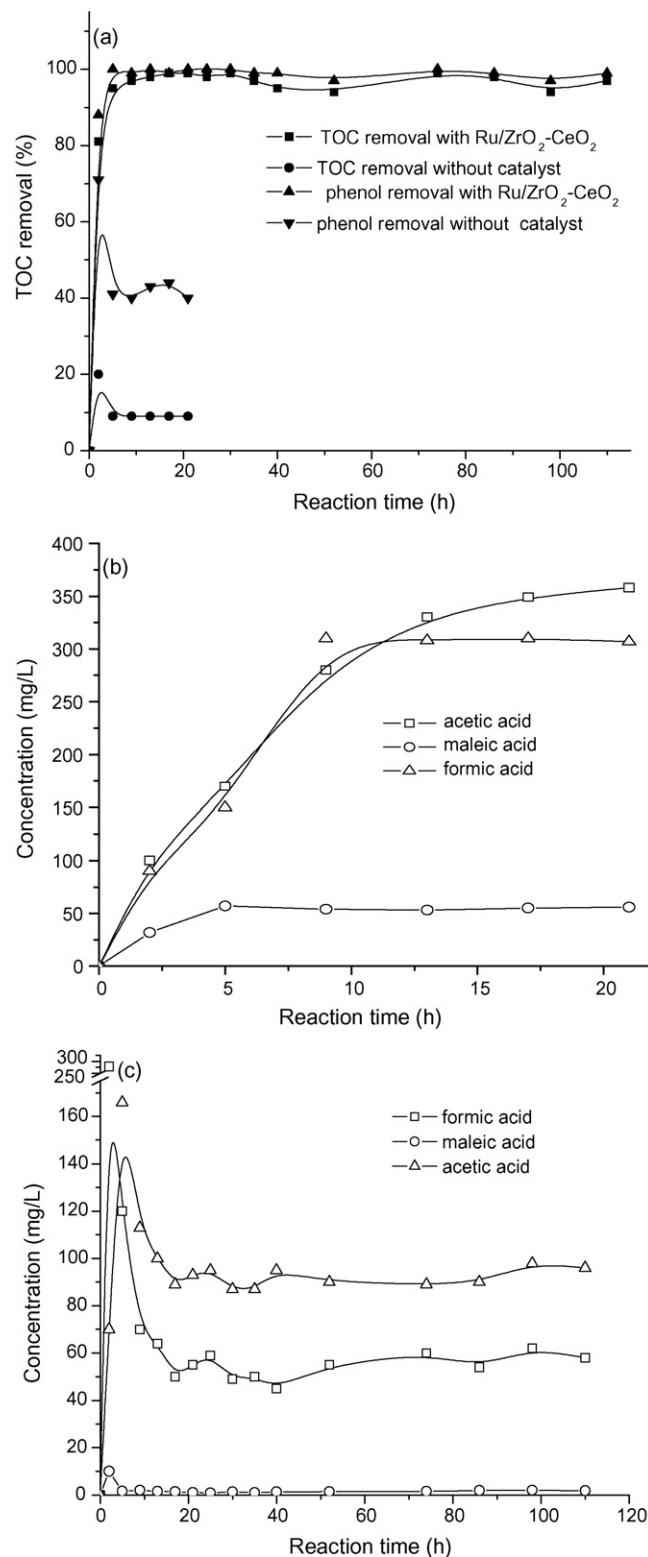


Fig. 4. TOC, phenol and carboxylic acid evolution in phenol oxidation with/without Ru/ZrO<sub>2</sub>-CeO<sub>2</sub>. (a) TOC and phenol with/without catalyst; (b) main carboxylic acids without catalyst; (c) main carboxylic acids with catalyst.



Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> and Ru/CeO<sub>2</sub>, respectively. Phenol is moderately adsorbed on both catalysts and the adsorption capacity of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> is a little higher than that of Ru/CeO<sub>2</sub>.

The XRD patterns of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> and Ru/CeO<sub>2</sub> were shown in Fig. 3. There is no obvious difference for main peaks between them. Both XRD patterns agree well with the presence of a cubic fluorite-type phase. All Miller indices are referenced to the unit cell in this structure. No peaks attributable to Ru were observed in both patterns, which is perhaps due to low content of Ru. X-ray fluorescence

spectrometer shows the pelletized ZrO<sub>2</sub>-CeO<sub>2</sub> has an average composition of Ce<sub>0.9</sub>Zr<sub>0.1</sub>O<sub>2</sub>. Actual Ru content of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> and Ru/CeO<sub>2</sub> was 1.8 and 1.7%, respectively. No peak attributable to Zr was observed in both patterns. It was reported that the introduction of ZrO<sub>2</sub> into CeO<sub>2</sub> lattice induced a structural modification in the material which brings the formation of a solid solution of composition Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> after calcination at high temperature [17]. However, there is no direct experiment proof for the formation of solid solution.

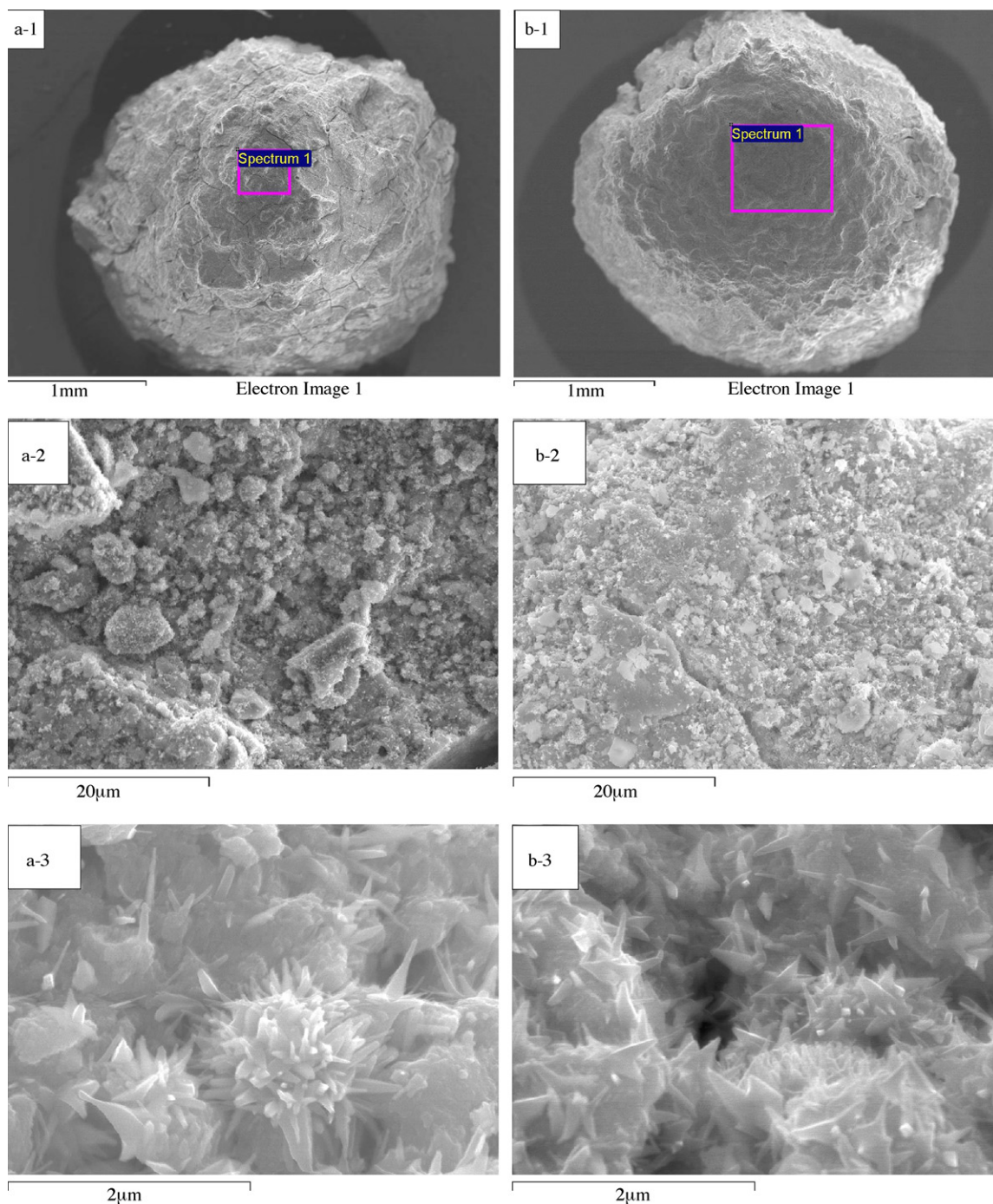


Fig. 5. SEM image of fresh catalyst and used catalyst. (a-1) fresh, 35 $\times$ ; (a-2) fresh, 2500 $\times$ ; (a-3) fresh, 30,000 $\times$ ; (b-1) used, 35 $\times$ ; (b-2) used, 2500 $\times$ ; (b-3) used catalyst, 30,000 $\times$ .

Table 1 also gives COD removal data after 120 min reaction with Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> and Ru/CeO<sub>2</sub> in the batch experiment for catalytic wet air oxidation of acetic acid. More information about catalytic wet oxidation with these two catalysts and the specific reaction condition was described in our previous work [20]. It can be concluded that Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> is a little more active than Ru/CeO<sub>2</sub> in catalytic wet air oxidation.

From the above discussion, it can be concluded that Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> is more applicable than Ru/CeO<sub>2</sub> in catalytic wet air oxidation. Therefore, pelletized Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> was selected as the catalyst used in our continuous experiment.

### 3.2. Catalytic wet air oxidation of phenol with Ru/ZrO<sub>2</sub>-CeO<sub>2</sub>

The results of wet air oxidation of phenol in a continuous packed-bubble column reactor are showed in Fig. 4. At the reaction of 0–5 h, the reactor is in the modulating period. The TOC and phenol removal is abnormal. After this period, the reactor operated stably. Without catalyst, TOC and phenol conversion stabilized around 9 and 42%, respectively. Generally in blank experiment, TOC and phenol conversion will be stable if reaction conditions are not changed. The blank experiment was carried out only for 21 h. With Ru/ZrO<sub>2</sub>-CeO<sub>2</sub>, TOC and phenol conversion stabilized around 96 and 100%, respectively for 100 h (Fig. 4a). Adding Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> can enhance TOC and phenol reduction greatly. During the phenol oxidation, many intermediates were produced. The main identified intermediates in experiment with Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> were maleic acid, acetic acid and formic acid. When the reactor operated stably, their concentrations stabilized around 5, 100 and 60 mg/L, respectively (Fig. 4c). In the blank experiment, their concentrations were about 50, 300 and 270 mg/L, respectively (Fig. 4b). It can be seen that the concentration of main carboxylic acids in effluent decreased greatly at the presence of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub>. In the blank experiment, some other intermediates such as oxalic acid, malonic acid and hydroquinone were found. The maximum leaching concentrations of ruthenium, zirconium and cerium during the reaction were 0.01, 0.005 and 0.04 mg/L, respectively. The leaching concentrations were all very low and the loss of catalytic activity of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> attributed to the leaching of active species would be little.

### 3.3. Comparison between fresh and used catalyst

As mentioned above, the using time of catalyst in the practical process is generally longer than 100 h. The comparison between fresh and used catalyst can bring some information about the stability of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> in the practical process.

After reaction, the Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts withdrawn from the reactor were not crushed. The morphologies of the fresh and used catalysts were studied by SEM. As shown in Fig. 5, for magnification 35×, the difference observed between the fresh and the used catalysts (Fig. 5 (a-1) and (b-1)) was not very significant. However, the SEM images with a magnification of

2500× (Fig. 5 (a-2) and (b-2)) show that the size of some granules became smaller. This change was perhaps caused by water trimming force in the reactor. The SEM images with a magnification of 30,000× (Fig. 5 (a-3) and (b-3)) reveal little difference. Moulijn et al. observed the formation of a filament mesh that covered the entire used catalyst through SEM analysis. They concluded that the formation of filaments was due to carbon in the catalyzed reactions of hydrocarbon [21]. Silva et al. also observed the formation of filament but they did not think those filaments were constituted by carbon [8]. For the catalysts in our experiments, there were carbon deposits on the surface of used catalyst, which will be demonstrated next, but the filaments were not observed.

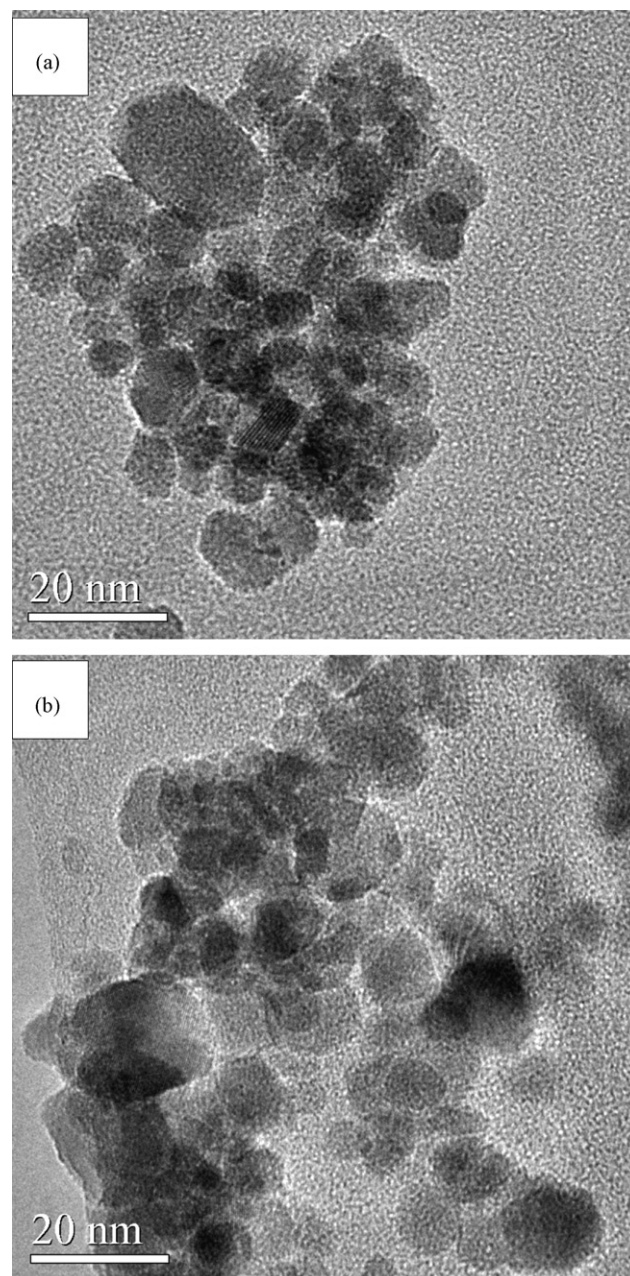


Fig. 6. TEM pattern of various catalysts. (a) Fresh Ru/ZrO<sub>2</sub>-CeO<sub>2</sub>; (b) used Ru/ZrO<sub>2</sub>-CeO<sub>2</sub>.



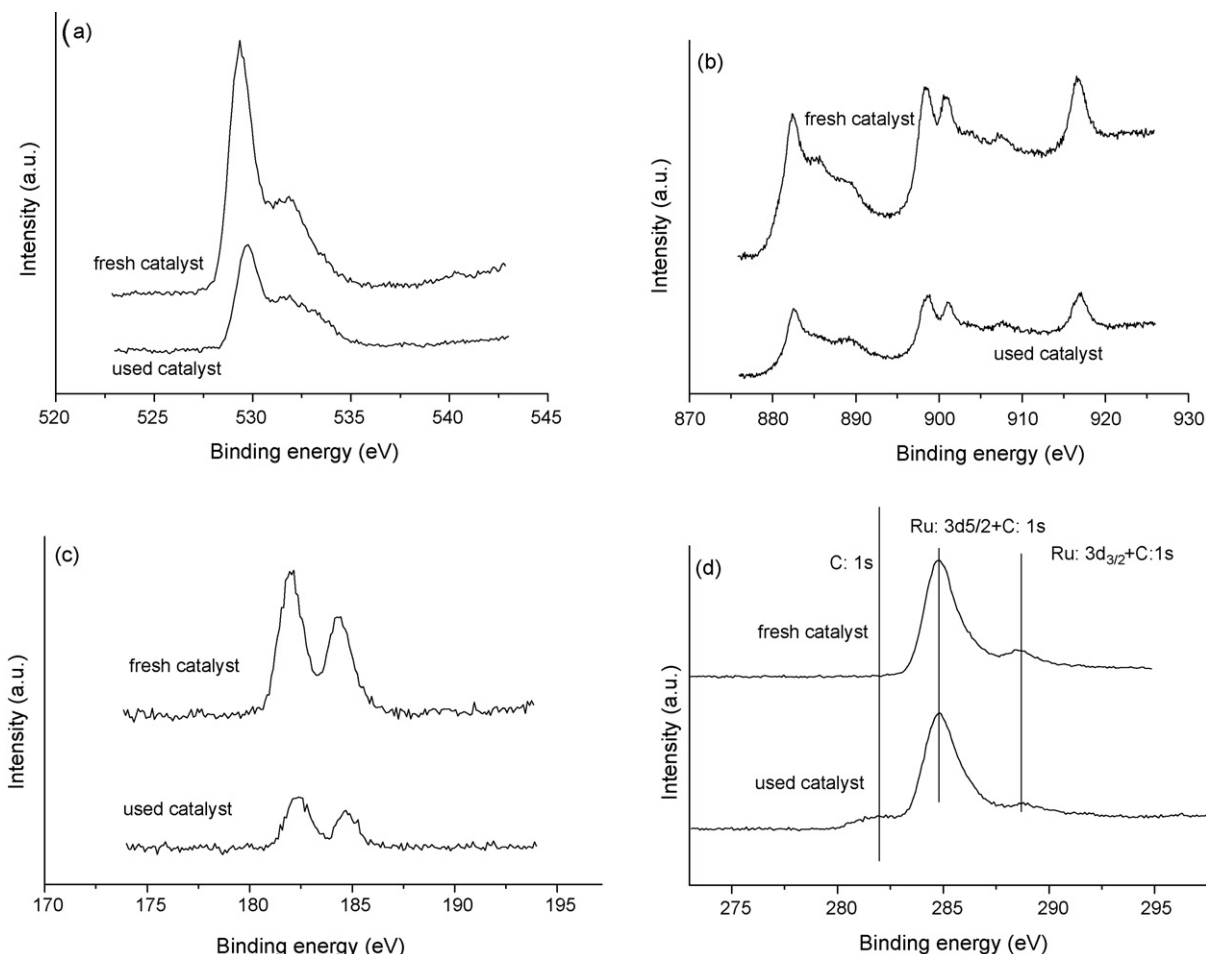


Fig. 7. XPS spectra of fresh and used catalyst. (a) O1s; (b) Ce3d; (c) Zr3d; (d) Ru3d + C1s.

Fig. 6 shows the typical TEM images of the fresh and used catalyst. No covering carbonaceous layer was observed on the samples. Delgado et al. [22] reported that a thick carbonaceous layer (20 nm) was observed in TEM image when there were carbonaceous deposits on the surface of Mn/Ce catalyst. The TEM micrographs shows the particle sizes were about 25 nm, indicating that the particle sizes did not change much during reaction. The particles of ruthenium and cerium were hardly discriminated by EDX in our experiment, though they were identified by Barbier et al. [5]. In our experiment, if the electron beam were converged to 25 nm, the intensity of excited X-ray of sample would be too weak to correctly identify ruthenium particles. Ru particles with size larger than 25 nm were not observed in our TEM experiment. As  $\text{ZrO}_2\text{-CeO}_2$  was first immersed in  $\text{RuCl}_3$  solution and then calcined at 300 °C in our experiment, Ru species in  $\text{Ru/ZrO}_2\text{-CeO}_2$  should be  $\text{RuO}_2$ .

The XRD results for the fresh and the used  $\text{Ru/ZrO}_2\text{-CeO}_2$  catalyst are shown in Fig. 3. The main peak of cubic fluorite-type phase did not change, and there were no other peaks occurring in the XRD pattern of used catalyst, indicating that the microcosmic crystal pattern did not change during reaction.

XPS has been successfully employed to provide useful surface analysis for many materials. It was used to probe the nature of the fresh and used catalyst in this study. Examination

of the spectra of a catalyst can help to determine the oxidation state of surface species. The spectra of Zr3d, Ce3d, Ru3d and O1s were undertaken for both fresh and used catalyst (Fig. 7). The observed lines did not shift, suggesting that the oxidation state of these species did not change during the reaction. In the spectra of fresh catalyst the O1s peak is asymmetric (the left is wider than the right) (Fig. 7a), indicating that there were different types of oxygen existed on the catalyst surface. The O1s peaks could be fitted into two peaks, referred to the lattice oxygen  $\text{O}_I$  and the chemisorbed oxygen  $\text{O}_{II}$  [23,24]. The O1s peak at about 529.0–530.0 eV could be attributed to the lattice oxygen  $\text{O}_I$  [24,25]. The peak at about 531.0 eV could be probably attributed to the chemisorbed oxygen  $\text{O}_{II}$  [23,24]. In the spectra of the used catalyst, the contribution of chemisorbed oxygen  $\text{O}_{II}$  increased, which was probably caused by accumulation of organic material on the surface of the used catalyst. In Fig. 7d, the spectra include not only the spectrum of Ru3d, but also the spectrum of the charging reference (C1s). In the spectra of fresh catalyst and used catalyst, there were two peaks at 284.80 and 288.69 eV, respectively, which were probably the overlapped peaks contributed to Ru3d and C1s [25]. In the spectrum of used catalyst, a new peak occurred at about 282.0 eV. It should be attributed to the C1s species different from those corresponding to the peaks at 284.80 and

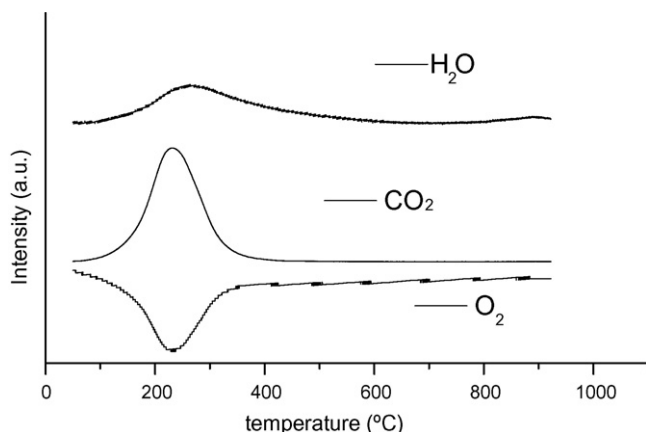


Fig. 8. TPO profile of used Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst.

288.69 eV. This also indicated that there were carbonaceous deposits on the surface of used catalyst.

Some references [26–28] also reported that many catalysts suffered from activity loss, which is frequently attributed to the formation of carbonaceous deposits on the surface of the catalyst. In order to get further insight into the nature of the carbonaceous deposits, TPO experiments were performed with the used catalysts. As shown in Fig. 8, oxygen consumption observed in the TPO experiment is linked to the burn-off carbonaceous materials. CO<sub>2</sub> and H<sub>2</sub>O are the unique products formed in this process. Through calculation from the amount of CO<sub>2</sub>, approximately 0.1% (w/w) C was adsorbed on the surface of used catalysts. Though the TOC, phenol and main carboxylic acids reduction with Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> were stable for 100 h reaction in the experiment, the catalytic activity of catalyst would decrease in experiment for longer time due to carbonaceous deposits. However, the carbonaceous deposits could be oxidized into CO<sub>2</sub> and H<sub>2</sub>O by oxidation at about 300 °C (Fig. 8). After this treatment, the catalyst perhaps could recover its initial catalytic activity.

#### 4. Conclusions

Introduction of ZrO<sub>2</sub> into CeO<sub>2</sub> can improve the mechanical strength, specific surface area and adsorption capacity of the pellets. Adding the pelletized catalyst of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> can enhance TOC, phenol and carboxylic acids reduction in catalytic wet air oxidation of phenol.

XPS spectra and TPO profile of the used catalyst reveal the formation of carbonaceous deposits on the surface of catalyst, which can cause catalytic activity loss in reaction for longer time. However, catalytic activity of the catalyst could be recovered through oxidation treatment at about 300 °C. The loss of catalytic activity of Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> caused by leaching of active species into acidic media was little. Ru/ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst has possibility of practical use.

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